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CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 24 June 2002 with an application for Letters Patent number 519744 made by VICTORIA LINK LTD.

Dated 7 July 2003.

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PROVISIONAL SPECIFICATION

IMPROVEMENTS IN OR RELATING TO WET OXIDATION

We, Victoria Link Limited, a New Zealand Company, of 15 Mount Street, Kelburn, Wellington, New Zealand, do hereby declare this invention to be described in the following statement:

TECHNICAL FIELD

5 The present invention relates to wet oxidation. A process is provided, by which organic or inorganic oxidisable material is subjected to an aqueous phase oxidation process to give oxidation products which are substantially in the vapour phase. Advantageously, the process is suitable for continuous operation. The process is particularly useful for the treatment of industrial waste

BACKGROUND ART

10

Wet oxidation is an effective method for lowering the chemical oxygen demand (COD) of many compounds. When applied to waste treatment processes, wet oxidation involves the aqueous phase oxidation of predominantly organic compounds at elevated temperatures and pressures. Temperatures of 127-300°C and pressures of 0.5-20 MPa are generally employed [1].

15

The vast majority of known processes relate to the wet oxidation of municipal sewage sludge [1].

20

The known processes all operate using the same general principles. A liquid or slurry is introduced into an autoclave *via* a pumping mechanism, and reacted with an oxidant under pressures and temperatures in the regions noted above. The products of the reaction are then removed from the reactor largely in the liquid phase, cooled, and separated outside of the reactor.

25

Oxygen is only sparingly soluble in water and its use as an oxidant requires the process to be operated at a pressure significantly above that of the vapour pressure of the liquid at the operating temperature, in order to minimise the loss of liquid inside the reactor. However, the use of high temperatures and pressures which necessitate the use of, for example: expensive alloys in the fabrication of reactors; costly valves; and significant safety measures; together with the long reaction times required, have limited the application of wet oxidation.

30

One approach which has been applied to overcome these obstacles is the use of an appropriate catalyst. If a catalyst is employed to increase the rate of reaction, a lower temperature, and correspondingly lower pressure, is generally required. However, typical catalysts comprise transition metal ions, the most effective of which are generally copper, manganese and iron. Due to their toxicity to other forms of life, these ions are restricted in terms of their disposal into public waterways. Therefore, strict disposal regulations apply to catalysts such as those based on transition metals.

Accordingly, the treated product from a wet oxidation reactor must have the concentration of the catalyst reduced to levels that satisfy the regulatory requirements. This may be achieved by, for example: precipitation as the hydroxide; pH modification to allow removal as the oxide; or a range of osmotic and electrochemical methods. All are costly and may be difficult to operate, thus limiting the use of catalysts in known processes.

Moreover, a mixture of compounds will usually be present in the waste stream to be treated and this further limits the known processes. The individual compounds generally have different rates of reaction, and therefore require different reactor residence times either in batchwise or continuous processes. This means that either:

- (a) the reactor residence time is limited to that of the compound within the mixture with the slowest rate of reaction, which generally dictates the use of a proportionally larger reactor; or
- (b) the process is less efficient and achieves a lower reduction in, for example, COD, biological oxygen demand (BOD) and percent conversion.

In addition, the more stable compounds which are correspondingly more difficult to oxidise may remain in the output stream from the reactor, and it is these compounds which are more likely to have detrimental environmental consequences.

These disadvantages have hindered the development of wet oxidation as a method for treating waste. Accordingly, it is an object of the present invention to provide a wet oxidation process which goes some way to overcoming these limitations, or at least provides the public with a useful choice.

SUMMARY OF INVENTION

In a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least
5 the steps of:

- (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- 10 (c) separating said vapour phase from said fluid phase.

) Generally the oxidisable material comprises an organic substance.

Preferably, the oxidisable material comprises a lipid, protein, carbohydrate, mineral oil,
15 vegetable oil, wax, hydrocarbon or a mixture thereof.

Optionally, the oxidisable material includes one or more oxidisable inorganic compounds.

Oxidants which may be used in a process of the invention include, but are not limited to
20 air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide.

) The temperature at which the process is operated is generally between 100 and 350°C and the pressure between 0.7 and 17.2 MPa.

25

Preferably, the temperature at which the process is operated is between 200 and 300°C, more preferably between 200 and 280°C.

Preferably, the pressure at which the process is operated is between 1.4 and 13.0 MPa,
30 more preferably between 2.0 and 3.5 MPa.

The process of the invention is particularly applicable to the treatment of industrial waste.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II), iron (II) or manganese (II) ions, or a mixture thereof.

- 5 Desirably, oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed.

The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present
10 invention provides a compound when produced by an oxidation process of the invention.

In a preferred embodiment, the compound is acetic acid, formic acid, carbon dioxide or a mixture thereof.

- 15 In another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

Although the present invention is broadly as defined above, those persons skilled in the art will appreciate that the invention is not limited thereto and that the invention also
20 includes embodiments of which the following description gives examples.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic diagram of apparatus particularly suitable for performing an
25 oxidation process of the invention on a laboratory scale.

Figure 2 is a schematic diagram of the additional modifications which may be made to the apparatus of Figure 1 to facilitate the treatment of slurries.

30 Figure 3 is a schematic diagram of a proposed pilot plant or commercial plant design.

Figure 4 is a graph of COD and temperature vs. time for the oxidation of glucose at 200°C in a process of the invention.

Figure 5 is a graph of pH and temperature vs. time for oxidation of glucose at 200°C in a process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

5

The present invention is broadly directed to the oxidation of various substances, conveniently described herein as "Phase Transfer Wet Oxidation".

10

Accordingly, in a first aspect, the present invention provides a process for oxidising a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

15

- (a) subjecting said feedstock to temperature and pressure to produce a fluid phase and a vapour phase;
- (b) contacting the feedstock of (a) with an oxidant to produce a vapour phase comprising at least some oxidation products; and
- (c) separating said vapour phase from said fluid phase.

20

The term "feedstock" as used herein includes, but is not limited to, aqueous liquids, solutions, suspensions, colloids, emulsions, and other mixtures. The term may also include substantially dry material to which is added a suitable aqueous liquid to form a slurry.

25

The amount of oxidisable material in the feedstock is typically less than about 10% by weight.

In one embodiment, the feedstock is fed directly into the apparatus. In an alternative embodiment, water is firstly introduced into the apparatus and then the oxidisable material is introduced into the apparatus.

30

The term "non-volatile" as used herein means that the oxidisable material is largely in the solid or liquid state under the temperature and pressure conditions in the reactor.

The term "contact" as used herein generally means admixing the aqueous solution or slurry with the oxidant in a suitable apparatus, hereinafter referred to as the "reactor", which is of a type designed to withstand the temperature and pressure and is well known in the art. Suitable reactors include, but are not limited to autoclaves and pressure reactors.

It will be appreciated that, preferably, the reactor is one in which the interfacial area between the oxidant and the feedstock is maximised, and from which the reaction products and the volatile non-oxidisable components present in the feedstock (for example, water) may be readily removed in the vapour phase.

The term "separate" as used herein generally means removing the vapour phase from the reactor while excluding the fluid phase.

In one embodiment, phase separation may be achieved by keeping the reaction pressure near to the vapour pressure of water at the reaction temperature by, for example, rapidly lowering the pressure of the reactor to remove volumes of treated material by flash vapourisation at specific intervals.

The aqueous solution or slurry may be introduced into the reactor by means of a pump or hydraulic plunger or by other means as are known in the art. Optionally, the apparatus may incorporate a means of stirring the contents, if and when required.

It will be appreciated that the temperature and pressure at which the process of the invention is operated are selected according to the stability or ease of oxidation of the feedstock. The temperature at which the process is operated is generally between 100 and 350°C and the pressure between 0.7 and 17.2 MPa.

Preferably, the temperature at which the process is operated is between 200 and 300°C, more preferably between 200 and 280°C.

Preferably, the pressure at which the process is operated is between 1.4 and 13.0 MPa, more preferably between 2.0 and 3.5 MPa.

The present invention also contemplates processes in which the feedstock is at the desired temperature and/or pressure prior to entering the reactor, for example a process in which the feedstock comprises a mixture of non-volatile oxidisable material and superheated steam.

5

Oxidants which may be used in a process of the invention include, but are not limited to: air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide. The oxidant is introduced into the reactor at an equivalent or greater pressure to that of the reactor and at a rate sufficient to effect oxidation.

10

Substances amenable to oxidation by a process of the invention are those which are relatively non-volatile under the temperature and pressure conditions at which the process is operated, and for which the major oxidation products are volatile under the same or similar conditions.

15

Generally the oxidisable material comprises an organic substance.

Preferably, the oxidisable material comprises a lipid, protein, carbohydrate (for example starch or cellulose), mineral oil, vegetable oil, wax, hydrocarbon or a mixture thereof.

20

It will be appreciated that some inorganic substances may be oxidised in a process of the invention. For example, phosphorus may be oxidised to phosphate in a process of the invention. Similarly, sulfur may be oxidised to sulfate and nitrogen to nitrate. Therefore, the oxidisable material may optionally include one or more oxidisable inorganic

25

compounds.

As explained in detail below, the process of the invention is particularly applicable to the treatment of industrial waste.

30 The term "treat" as used herein means that the chemical oxygen demand (COD) or biological oxygen demand (BOD) of the waste stream is reduced.

Suitable waste streams for treatment in a process of the invention include consumer and industrial waste streams including, but not limited to:

- dairy shed waste, for example "cow dung" from milking shed wash downs;
- pig and chicken waste;
- milk, cheese and butter vat wash downs, from milk processing plants;
- food processing wastes, for example from the washing and preparation of vegetables, and
- 5 waste from the wine industry and brewing industry;
- food waste;
- shipboard waste;
- waste from environmentally sensitive locations;
- mineral oils, for example from the wash downs and oil-traps of petroleum service stations
- 10 and garages;
- waste fats and proteins from the meat processing industry, for example abattoir
- stickwater;
- wool-scouring waste;
- sewage;
- 15 medical waste;
- fibre, ink and polymeric material from the deinking waste produced in the recycling of
- paper;
- waste paper and paper products;
- waste wood and wood products;
- 20 other waste products from the wood processing industries including wood fibre, saw dust
- and wood treated with preservatives;
- rubber waste;
- plastic waste; and
- tannin and other colorants from wood pulping streams

25

Similarly, other waste treatment applications in which a process of the invention may be employed include, but are not limited to:

reclamation of sites contaminated by organic materials including at least petrochemical, gas works, timber treatment or agrochemical sites; and

30 recovery of inorganic preservatives from wood.

While the oxidisable substances are non-volatile, their primary wet oxidation products are generally volatile compounds such as carbon dioxide, acetic acid, and formic acid. It will therefore be understood that while the feedstock is introduced to the reactor in the liquid

or solid phase, the products of the oxidation reaction may be removed from the reactor in the vapour phase, hence the name "Phase Transfer Wet Oxidation".

5 Accordingly, a significant portion of the oxidation products from a process of the invention is removed in the gas phase. This is in contrast to the known processes in which the reaction products are generally removed in the liquid phase.

10 It will be appreciated that any compound which is volatile at the reaction temperature may be present in the gas phase. However, any higher molecular weight compounds, such as higher organic acids, will generally be present at very low concentrations.

) The oxidation products in the separated vapour phase may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides a compound when produced by an oxidation process of the invention.

15 Typical compounds include, but are not limited to, carbon dioxide, formic acid, acetic acid, higher organic acids and mixtures thereof.

In a preferred embodiment, the compound is acetic acid, formic acid, carbon dioxide or a mixture thereof.

) More preferably, the compound is acetic acid or a mixture of acetic acid and formic acid. The acetic acid so provided is sterile. Accordingly, the acetic acid may be converted to acetate and utilised as a nutrient source for microorganisms.

25 Advantageously, the temperature and pressure of the vapour phase is reduced in a heat exchanger and the heat recycled to the incoming feedstock. In another embodiment, the incoming feedstock and the reaction mix are optionally heated by the addition of external heat.

30 Desirably, oxidation may be carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed.

When the oxidation is carried out as a continuous process the reactor will advantageously incorporate a means of measuring the fluid level within the reactor, such that the reactor does not run dry.

5 If a mixture of oxidisable substances is subjected to a process of the invention, then those with a faster rate of reaction will oxidise first, and the products of the reaction are removed in the vapour phase as they are formed. More stable substances, with a correspondingly slower rate of reaction, will remain in the reactor until they have oxidised to volatile products. Any water in the feedstock entering the reactor will also be
10 vapourised, thereby permitting more feedstock to enter the reactor. This is in contrast to the known processes, which require either a large reactor, or provide a reduction in the percent conversion of oxidisable substances to their oxidation products.

Optionally, a catalyst may be employed to increase the rate of reaction. Suitable catalysts
15 include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II), iron (II) or manganese (II) ions, or a mixture thereof.

While it will be appreciated that the process of the invention is amenable to heterogeneous catalysis, the catalyst may advantageously be in the form of an
20 homogenous catalyst. In the known processes, the use of homogenous catalysts generally leads to catalyst leaching and subsequent contamination of the downstream products. However, it will be appreciated that, in a process of the present invention, the catalyst may remain in the dissolved liquid phase in the reactor. In this way an initial amount of catalyst may be introduced into the reactor, where it will remain while multiple volumes
25 of feedstock are introduced into the reactor and the oxidation products removed in the vapour phase.

Thus, the catalyst does not need to be replaced until the entire reactor is emptied, for example for cleaning, or unless a feedstock with a high salt content is being treated. For
30 feedstocks with a high salt content, the non-volatile salts accumulate inside the reactor, which may require a "flush" cycle as the solubility limit of the least-soluble salt begins to be reached and the effective reactor volume decreases.

Desirably, any useful non-volatile salts which accumulate in the reactor may be recovered. In one embodiment, applying a process of the invention to the treatment of tanalised wood waste will lead to an accumulation of copper chrome arsenate in the reactor which may be recovered and recycled. In an alternative embodiment, phosphate, sulfate and nitrate salts resulting from the oxidation of proteins in a process of the invention will accumulate in the reactor and may precipitate when their saturation solubility is exceeded. Advantageously, the concentrated solution or precipitated salts may be used for other applications, for example as fertilizer.

- 10 Accordingly, in another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

Those persons skilled in the art will appreciate that there is a relationship between the internal volume of the reactor and the volume of feedstock that may be treated by means of Phase Transfer Wet Oxidation before the system is flushed and the process restarted. This ratio may be conveniently referred to as the "Batch Ratio".

It will be appreciated that unless external heat is applied, the heat-balance of the overall reaction must be great enough to compensate for the enthalpy of vapourisation at the reactor operating temperature, along with the energy required to bring the feedstock to that temperature. Heat will be recovered from the exothermic nature of the reaction and may also be recovered, *via* a cool-down heat exchanger, from the vapour phase as it is removed from the reactor. This is summarised in Equation 1.

25 EQUATION 1

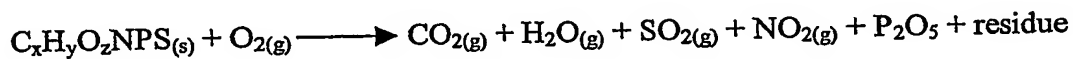
$$Q = \Delta H_{\text{rxt}} + E_{\text{recyc}} - E_{\text{temp}} - \Delta H_v = \Delta H_{\text{rxt}} + E_{\text{recyc}} - mc\Delta T - m\Delta H_v \geq 0$$

where ΔH_{rxt} is the enthalpy of reaction, E_{recyc} the energy recovered from the cool-down heat exchanger, E_{temp} the energy required to raise the feedstock to the desired operating temperature, ΔH_v the heat of vaporisation of the liquid at the operating temperature, m the mass of feedstock, c the specific heat of the feedstock, and ΔT the difference between the feedstock and operating temperatures.

The pollution potential for a waste stream is often measured in terms of its COD which equates to the mass of oxygen required to convert the sample from its original "high energy state" to carbon dioxide and water. A similar measurement provides the BOD which equates to the mass of oxygen consumed by a standard biological organism (generally a species of bacteria) as it uses the waste stream as a nutrient source. Thus, an effective measure of the extent to which a sample has been degraded, and one which is often used as a legal means of classification into "acceptable" and "unacceptable" waste streams, is the difference between the COD and/or BOD of the sample before and after processing.

For thermal combustion at atmospheric pressure, where the oxidant is in the gas phase, the reactants are converted to, *inter alia*, carbon dioxide, water, sulfur dioxide, nitrogen dioxide, phosphorus pentoxide and sulfur dioxide (Equation 2).

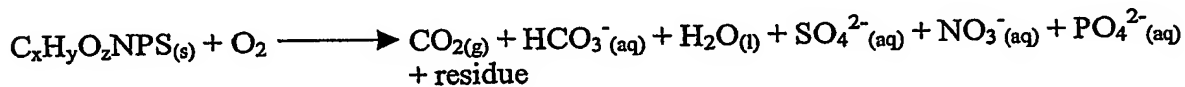
EQUATION 2



While often utilised in the past as a disposal method, thermal combustion has lost favour due to venting of the gases produced to the atmosphere. In addition, the reactants must be sufficiently dry to allow the combustion to be self-sustaining.

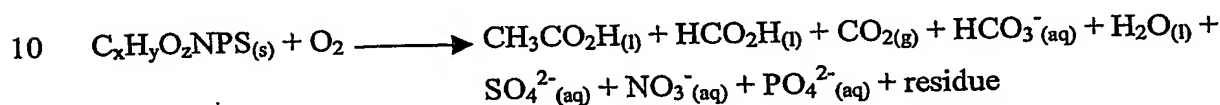
In contrast to thermal combustion, wet oxidation utilises dissolved oxygen at elevated pressures and temperatures to carry out the oxidation. However, the products of the oxidation of nitrogen, phosphorus and sulfur, for example, are kept in the liquid phase with sulfur as sulfate, nitrogen as nitrate and phosphorus as phosphate (Equation 3). A portion of the carbon is oxidised to carbon dioxide and dissolves in the liquid phase to form carbonate/bicarbonate ions.

EQUATION 3



Thus, the theoretical products of wet oxidation are carbonate/bicarbonate and water, plus any inorganic ions, generally oxy-anions, resulting from the presence of other elements in the oxidisable material. However, in practice the reaction does not convert the entire initial carbon loading to carbonate/bicarbonate. Instead, quantities of acetic and formic acids are formed (Equation 4) and much lower levels of higher molecular weight organic acids.

EQUATION 4



These acids are generally the major products of reaction, and thus the primary source of COD and BOD in the products.

An analysis of the phase diagram of acetic acid in water at the temperatures and pressures associated with wet oxidation, shows that the concentrations of this compound in the vapour phase and the liquid phase are almost identical. These data are presented in Table 1, Table 2 and Table 3. Formic acid behaves in a similar manner. Therefore, as the oxidisable substances are non-volatile under the conditions generally used for wet oxidation and the products of the reaction (principally acetic acid, formic acid, water and carbon dioxide) are volatile under these conditions, the two may be separated.

This contrasts with the known processes, wherein both the *untreated* waste stream (the feedstock) and the *treated* stream (the products) are generally in the liquid phase.

TABLE 1 Acetic acid concentrations (10% w/w in water initially) in the vapour phase ¹

| <i>Temp. (°C)</i> | <i>Pressure (kPa)</i> | <i>Acetic acid (%w/w)</i> |
|-------------------|-----------------------|---------------------------|
| 160 | 551 | 5.0 |
| 180 | 965 | 7.4 |
| 200 | 1516 | 8.0 |
| 220 | 1964 | 8.2 |
| 240 | 3032 | 8.1 |
| 260 | 4272 | 8.1 |
| 280 | 5684 | 8.2 |
| 300 | 7441 | 8.8 |

TABLE 2 Acetic acid concentrations (20 % w/w in water initially) in the vapour phase ¹

| <i>Temp. (°C)</i> | <i>Pressure (kPa)</i> | <i>Acetic acid (%w/w)</i> |
|-------------------|-----------------------|---------------------------|
| 160 | 655 | 14.1 |
| 180 | 1034 | 17.5 |
| 200 | 1516 | 17.3 |
| 220 | 1998 | 18.9 |
| 240 | 3032 | 17.5 |
| 260 | 4237 | 18.0 |
| 280 | 5753 | 18.5 |
| 300 | 7441 | 18.0 |

TABLE 3 Acetic acid concentrations (40 % w/w in water initially) in the vapour phase ¹

| <i>Temp. (°C)</i> | <i>Pressure (kPa)</i> | <i>Acetic acid (%w/w)²</i> |
|-------------------|-----------------------|---------------------------------------|
| 160 | 620 | 29.8 |
| 180 | 896 | 32.6 |
| 200 | 1550 | 33.0 |
| 220 | 2101 | 36.1 |
| 240 | 3032 | 37.3 |
| 260 | 3858 | 37.6 |
| 280 | 5581 | 39.0 |
| 300 ³ | 6787 | 43.2 |

¹ 1 L samples in the 2 L autoclave. For the 20 & 40% w/w runs, the samples were purged with argon for 10 minutes prior to heating. ² Estimated using integrations of the ¹H n.m.r. exchangeable and non-exchangeable peaks. ³ Liquid removed after run was a dark-brown colour, indicating possible decomposition and carbonisation of the initial acid.

EXPERIMENTAL

EXAMPLE 1

5 Glucose

Glucose is similar to the constituents of many industrial waste streams, in particular cellulose and starch. In addition, glucose is readily oxidisable, and the products of reaction easily analysed. Therefore it is an ideal model compound.

10

Method

The apparatus shown in Figure 1 was used for this Example. A 1% (w/v) solution of glucose was pumped at a rate of 8 mL.min⁻¹ into an autoclave (a Parr Stirred Pressure
15 Reactor Vessel of 2 L capacity, of which less than 400 mL was used at any one time), the autoclave having been pre-filled with 300 mL of the aforesaid glucose solution. Air was introduced from a standard gas cylinder at a rate of approximately 15 standard cubic feet per hour (SCFH), measured on the outlet line from the reactor. This is significantly more than that required to effect the oxidation of the glucose solution, but was deemed
20 necessary due to the poor mixing observed in the small reactor. The reactor was stirred by means of a motor-driven rod with stirring blades submerged below the liquid level, and rotated at a rate of 600 rpm.

The reactor was heated electrically to a temperature of 200°C, and the temperature kept at
25 this level by means of a thermostat-led control system.

The outlet port was connected to a cooling bath and liquid trap, whereby the reaction products could be removed as required. The pressure and flow of gas through the outlet port was controlled *via* a back-pressure regulator coupled to a pressure gauge. Carbon
30 dioxide, nitrogen, and unreacted oxidant passed through this regulator, the pressure dropped to ambient, and the gas flow on the outlet side measured before venting the gases to atmosphere.

A summary of the reaction conditions used in this Example are listed in Table 4.

TABLE 4 Summary of Conditions Used in the Treatment of Glucose

| Component | Value | Units |
|------------------------------|-------|----------------------|
| Pressure at tank (regulator) | 2.76 | MPa |
| Pressure in reactor | 2.62 | MPa |
| Back pressure regulator | 2.21 | MPa |
| Reaction temperature | 200 | °C |
| Pumping rate (feedstock) | 8.00 | mL.min ⁻¹ |
| Stirring speed | 600 | Rpm |
| Oxidant flow | 15 | SCFH (air) |
| Reactor volume (total) | 2000 | mL |
| Reactor volume (utilised) | 300 | mL |

5 Results

The chemical oxygen demand (COD), pH, and low molecular weight organic acids produced were analysed. These are listed in Table 5, Table 6 and Table 7. The results show that the process was able to be operated with the feedstock (glucose solution) being continuously added to the reactor, and the products of reaction (primarily acetic acid, formic acid and carbon dioxide) being continuously withdrawn from the reactor in the vapour phase, before being condensed to ambient temperature.

The COD of both the feedstock (glucose) and the products (primarily water, acetic and formic acids) were measured throughout the experiment and the results are presented in Table 6. The feedstock COD (COD_i) was constant at 10.3 g.L⁻¹, while the COD of the treated stream (COD_f) varied between 0.65 and 2.23 g.L⁻¹. The change in temperature and in the COD of the treated stream with respect to time is represented graphically in Figure 4.

20

A total of 6.40 g COD (as glucose) was added to the reactor. The product stream had a total COD of 1.56 g which is a reduction of 75.6 % from that of the untreated glucose (see Table 7). The pH of the treated stream withdrawn in the vapour phase was measured and these data are presented in Table 5. The pH of the treated stream decreased to approximately 3, consistent with the formation of the low molecular weight organic acids. The change in temperature and in the pH of the treated stream withdrawn in the vapour phase with respect to time is represented graphically in Figure 5.

25

Table 6 also shows the volume of product removed at each stage in the reaction which was typically $7 \text{ mL} \cdot \text{min}^{-1}$, though a large variation was noted due to the equipment used. It is unlikely that such a variation would exist in a scaled-up process.

5 **TABLE 5** Low Molecular Weight Organic Acids Produced in the Oxidation of Glucose at 200°C

| <i>Min</i> | <i>Acetic (mg.L⁻¹)</i> | <i>Formic (mg.L⁻¹)</i> | <i>pH</i> |
|------------|-----------------------------------|-----------------------------------|-----------|
| 0 | 0 | 0 | 7.30 |
| 31 | 42 | 196 | 3.72 |
| 40 | 316 | 107 | 3.14 |
| 65 | 586 | 224 | 2.91 |
| 93 | 486 | 2129 | 2.85 |
| 120 | 340 | 1030 | 2.86 |
| 180 | 308 | 1162 | 2.90 |
| Post run | 511 | 5755 | 2.64 |

10 **TABLE 6** Reduction of COD in the Oxidation of Glucose

| <i>Min</i> | <i>°C</i> | <i>V_{out}</i> (<i>mL/min</i>) | <i>COD_i</i> (<i>g/L</i>) | <i>COD_f</i> (<i>g/L</i>) | <i>Red (%)</i> <i>in COD</i> |
|------------|-----------|---------------------------------------------|------------------------------------------|------------------------------------------|---------------------------------|
| 0 | 25 | 0.0 | 10.34 | - | - |
| 10 | 60 | 0.0 | - | - | - |
| 28 | 193 | 0.0 | - | - | - |
| 31 | 200 | 16.5 | 10.34 | 0.65 | 93.8 |
| 40 | 195 | 8.5 | 10.34 | 1.53 | 85.2 |
| 65 | 198 | 7.0 | 10.34 | 2.03 | 80.4 |
| 93 | 190 | 4.0 | 10.34 | 2.23 | 78.4 |
| 120 | 204 | 4.4 | 10.34 | 2.11 | 79.6 |
| 180 | 203 | 1.5 | 10.34 | 2.23 | 78.4 |
| Post run | - | 102.9 | 10.34 | 3.51 | 66.1 |

TABLE 7 Summary of the Oxidation of Glucose

| <i>Component</i> | <i>Result</i> |
|-----------------------------|---------------|
| Total COD in | 6.40 g |
| Total COD out | 1.56 g |
| Reduction in COD | 4.84 g |
| Percentage reduction in COD | 75.6 % w/w |

EXAMPLE 2

Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)

5 Commercial lard is similar to the constituents of many waste streams from the dairy and meat processing industries. It is not readily oxidisable under ambient conditions, and generally requires a catalyst to achieve a significant reduction in chemical oxygen demand at temperatures below 270°C . Standard batch runs were carried out with an equivalent sample (stickwater from a local abattoir) both with and without a catalyst to
10 illustrate this. It was found that *without* a catalyst, a temperature of 280°C was required to achieve a reduction in COD of 78 %. At 230°C , a catalyst concentration of $100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$ gave a reduction in COD of 69 %, while at a concentration of $1000 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$ (see Example 3) a reduction in COD of 83 % was achieved. However, when *no* catalyst was used at the same temperature (230°C), the reduction in COD was
15 limited to approximately 55 %.

Method

The experimental apparatus shown in Figure 1 with the modification shown in Figure 2
20 was used for this Example. An emulsion of lard in water (approximately 1% w/v) was pumped at a rate of 8 mL/min into an autoclave (2 L capacity, of which less than 400 mL was used at any one time) the autoclave having been pre-filled with 300 mL of water containing $100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$ (as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Pumping of the emulsion was not started until the reactor had reached operating temperature (230°C) after which it was kept at this
25 level by means of a thermostat controlled system. Air was introduced from a standard gas cylinder at a rate of approximately 11 ± 2 standard cubic feet per hour (SCFH), measured on the outlet line from the reactor. This is significantly more than that required to effect the oxidation of the lard solution, but was deemed necessary due to the poor mixing observed in the small reactor. The reactor was stirred by means of a motor-driven rod
30 with stirring blades submerged below the liquid level, and rotated at a rate of 600 rpm.

The outlet port was connected to a cooling bath and liquid trap, whereby the reaction products could be removed as required. The pressure and flow of gas through the outlet

port was controlled *via* a back-pressure regulator coupled to a pressure gauge. Carbon dioxide, nitrogen, and unreacted oxidant passed through this regulator, the pressure dropped to ambient, and the gas flow on the outlet side measured before venting the gases to atmosphere.

5

A summary of the reaction conditions used in this Example are listed in Table 8.

TABLE 8 Summary of Conditions Used in the Oxidation of Commercial Lard with 100 mg.kg⁻¹ Cu²⁺

10

| Component | Value | Units |
|---------------------------------------|--------|----------------------|
| Pressure at tank (regulator) | 3.31 | MPa |
| Pressure in reactor | 3.17 | MPa |
| Back pressure regulator | 3.03 | MPa |
| Reaction temperature | 230 | °C |
| Pumping rate (feedstock) ¹ | 8.00 | mL.min ⁻¹ |
| Stirring speed | 600 | rpm |
| Oxidant flow | 11 ± 2 | SCFH (air) |
| Reactor volume (total) | 2000 | mL |
| Reactor volume (utilised) | 300 | mL |

¹Pumping not started till time = 51 min (when operating temperature was reached).

Results

15

The results of the phase-transfer wet oxidation of commercial lard with 100 mg.kg⁻¹ Cu²⁺ are shown in Table 9, Table 10, Table 11 and Table 12.

20

The results show that a sample of lard (as an emulsion in water) could be continuously pumped into the reactor, while at the same time the products of reaction could be continuously removed in the vapour phase and cooled in a heat-exchanger before exiting the system. Further to this, an initial dose of catalyst at a concentration of 100 mg.kg⁻¹ could treat the entire sample, and provide a reduction in COD greater than that able to be achieved in the absence of a catalyst. It should also be noted that while 100 mg.kg⁻¹ of catalyst was used, if this is recalculated over the entire treated volume, it then equates to 22.5 mg.kg⁻¹.

25

The COD of both the untreated and treated streams were measured throughout the course of the reaction and the results are presented in Table 10. The (untreated) emulsion of lard in water had a constant COD of 5476 mg.kg⁻¹, while the treated products had a COD in the order of approximately 1000 mg.kg⁻¹. In total, the feedstock had a total COD of 5.65 g, while the treated stream had a total COD of 1.99 g which is a reduction of 64.7 % (see Table 12).

As shown in Table 9, the pH of the treated stream dropped from 6.67 to 2.84 during the course of reaction which is consistent with the formation of formic and acetic acids. The concentration of these acids was also measured during the course of the reaction and the results are presented in Table 11. The concentration was found to be in the order of 70 mg.kg⁻¹ for both acetic and formic acid.

TABLE 9 Oxidation of Lard (100 mg.kg⁻¹ Cu²⁺) - pH, Temperature and Condensate Volumes

| <i>Time (min)</i> | <i>Temp (°C)</i> | <i>V_{out} (mL)</i> | <i>pH</i> |
|-----------------------------|------------------|-----------------------------|-----------|
| 0 | 18 | | 8.70 |
| 60 | 225 | 170.0 | 6.67 |
| 70 | 227 | 100.1 | 4.60 |
| 80 | 235 | 50.5 | 3.70 |
| 90 | 223 | 39.4 | 3.58 |
| 100 | 227 | 39.6 | 3.50 |
| 120 | 227 | 92.4 | 3.62 |
| 150 | 225 | 116.3 | 3.18 |
| 180 | 227 | 176.4 | 2.84 |
| <i>Vol left in reactor:</i> | | 154.0 | 2.46 |

¹ Sample taken from inlet line to reactor

TABLE 10 Oxidation of Lard (100 mg.kg⁻¹ Cu²⁺) - COD data

| <i>Time (min)</i> | <i>COD (mg.L⁻¹)</i> |
|-------------------|--------------------------------|
| Untreated | 5476 |
| 60 | 2600 |
| 120 | 634 |
| 180 | 970 |
| Post run | 4214 |

TABLE 11 Oxidation of Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$) - Formic and Acetic acid Concentrations

| <i>Time (min)</i> | <i>Acetic (mg.L⁻¹)</i> | <i>Formic (mg.L⁻¹)</i> |
|-------------------|-----------------------------------|-----------------------------------|
| Pre-run | 32 | 50 |
| 60 | 80 | 63 |
| 70 | 62 | 70 |
| 80 | 68 | 80 |
| 90 | 85 | 91 |
| 100 | 100 | 90 |
| 120 | 99 | 82 |
| 150 | 101 | 89 |
| 180 | 120 | 116 |
| Post-run | 216 | 211 |

5 TABLE 12 Summary of Results in the Oxidation of Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)

| <i>Component</i> | <i>Result</i> |
|-----------------------------|-------------------------|
| Total COD in | 5.65 g |
| Total COD out | 1.99 g |
| Reduction in COD | 3.66 g |
| Percentage reduction in COD | 64.7 % w/w |
| Total volume treated | 1332 mL |
| Lost as vapour | 393 mL |
| Batch ratio | > 4.4 (based on 300 mL) |

EXAMPLE 3

10 Lard ($1000 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)

Method

The method used was identical to that for Example 2 (Lard ($100 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$)) except that $1000 \text{ mg.kg}^{-1} \text{ Cu}^{2+}$ was used as the catalyst. As with Example 2, the experimental apparatus used was also that shown in Figure and Figure 2.

A summary of the reaction conditions used in this Example are listed in Table 13.

TABLE 13 Summary of Conditions Used in the Oxidation of Commercial Lard with 1000 mg.kg⁻¹ Cu²⁺

| Component | Value | Units |
|---------------------------------------|-------|----------------------|
| Pressure at tank (regulator) | 3.24 | MPa |
| Pressure in reactor | 3.17 | MPa |
| Back pressure regulator | 3.03 | MPa |
| Reaction temperature | 230 | °C |
| Pumping rate (feedstock) ¹ | 8.00 | mL.min ⁻¹ |
| Stirring speed | 600 | Rpm |
| Oxidant flow | 8 | SCFH (air) |
| Reactor volume (total) | 2000 | mL |
| Reactor volume (utilised) | 300 | mL |

5 ¹Pumping not started till operating temperature was reached (denoted t=0).

Results

10 The results are presented in Table 14, Table 15 and Table 16. These show that when the initial dose of catalyst is increased to 1000 mg.kg⁻¹ a reduction in COD of 83 % may be achieved, with the same concentration of catalyst treating approximately 5.8 volumes of waste. It should be noted that the volume treated was limited only by the equipment available, in particular the size of the hydraulic plunger used to transfer the feedstock into the autoclave. In practice the volume able to be treated by a single dose of catalyst would
15 be many times greater than that achieved here.

) Samples were withdrawn at periodic intervals from the treated stream and their COD and volume measured. The sample volumes are shown in Table 14 and the COD in Table 15. The volume of the treated stream was slightly less than that pumped in, due to the partial
20 loss of carbon dioxide as vapour from the reaction. Additionally, the oxidant used was dry air from a compressed cylinder, which upon leaving the reaction would have taken up a small volume of water.

The COD of the feedstock was constant at 6850 mg.kg⁻¹ while that of the treated products
25 was found to be approximately 1400 mg.kg⁻¹.

Overall, the feedstock had a total COD of 9.90 g, while the products recovered had total COD of 1.68 g which is a reduction of 83 % (see Table 16).

TABLE 14 Oxidation of Lard¹ at 230°C with 1000 mg.kg⁻¹ Cu²⁺

| <i>Time (min)</i> | <i>Temp (°C)</i> | <i>Vol out (mL)</i> |
|----------------------|------------------------------------------------------|---------------------|
| 0 | sample taken from inlet line to reactor ² | |
| 10 | 225 | 86.3 |
| 20 | 225 | 77.2 |
| 30 | 227 | 55.8 |
| 45 | 227 | 105.9 |
| 60 | 225 | 101.1 |
| 90 | 225 | 227.8 |
| 120 | 225 | 200.0 |
| 150 | 227 | 227.3 |
| 180 | 227 | 216.6 |
| Vol left in reactor: | | 154.0 |

¹300 mL H₂O initially in the reactor, with 1.20 g CuSO₄.5H₂O (1000 mg.kg⁻¹ Cu²⁺). Reactor brought to 230°C before pumping from the hydraulic plunger began. ²i.e. this equates to the untreated sample.

TABLE 15 Oxidation of Lard (100 mg.kg⁻¹ Cu²⁺) - COD data

| <i>Time (min)</i> | <i>COD (mg.L⁻¹)</i> |
|-------------------|--------------------------------|
| 0 | 6850 |
| 10 | 1190 |
| 20 | 1190 |
| 30 | 1190 |
| 45 | 1400 |
| 60 | 1400 |
| 90 | 1480 |
| 120 | 1250 |
| 150 | 1220 |
| 180 | 1220 |
| Post-run | 2020 |

TABLE 16 Summary of Results in the Oxidation of Lard (1000 mg.kg⁻¹ Cu²⁺)

| <i>Component</i> | <i>Result</i> |
|-----------------------------|-----------------------|
| Total COD in | 9.90g |
| Total COD out | 1.68 g |
| Reduction in COD | 8.19 g |
| Percentage reduction in COD | 83.0 % w/w |
| Total volume treated | 1740 mL |
| Lost as vapour | 288 mL |
| Batch ratio | 5.8 (based on 300 mL) |

INDUSTRIAL APPLICATION

It will be appreciated that, in use, the present invention provides a process for oxidising a feedstock which may be applied to the treatment of industrial waste. Advantageously, the reactor may be of a significantly smaller volume than that used in known processes due to the removal of both water and easily oxidisable compounds from the reactor in the vapour phase, allowing for further feedstock to enter the system. In this way the process may be operated in a continuous manner.

In addition, an homogenous catalyst may be used for more stable compounds, and the catalyst retained in the reactor while multiple volumes of waste were treated. A variety of consumer and industrial waste streams are amenable to treatment by a process of the invention, and these are discussed above.

Furthermore, the present invention also provides a sterile source of, for example, acetic acid which may be utilised, following conversion to acetate, as a nutrient source for microorganisms.

Those persons skilled in the art will further appreciate that the present description is provided by way of example only and that the scope of the invention is not limited thereto.

REFERENCES

1. Kolackowski, S., Plucinski, P., Beltran, F., Rivas, F., McLurgh, D. "Wet air oxidation: a review of process technologies and aspects in reactor design", *Chem. Eng. J. (Lausanne)*, 1999, 73, 2, 143-160.

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By the authorized agents

A J TINK

for

Guillaume de Grest

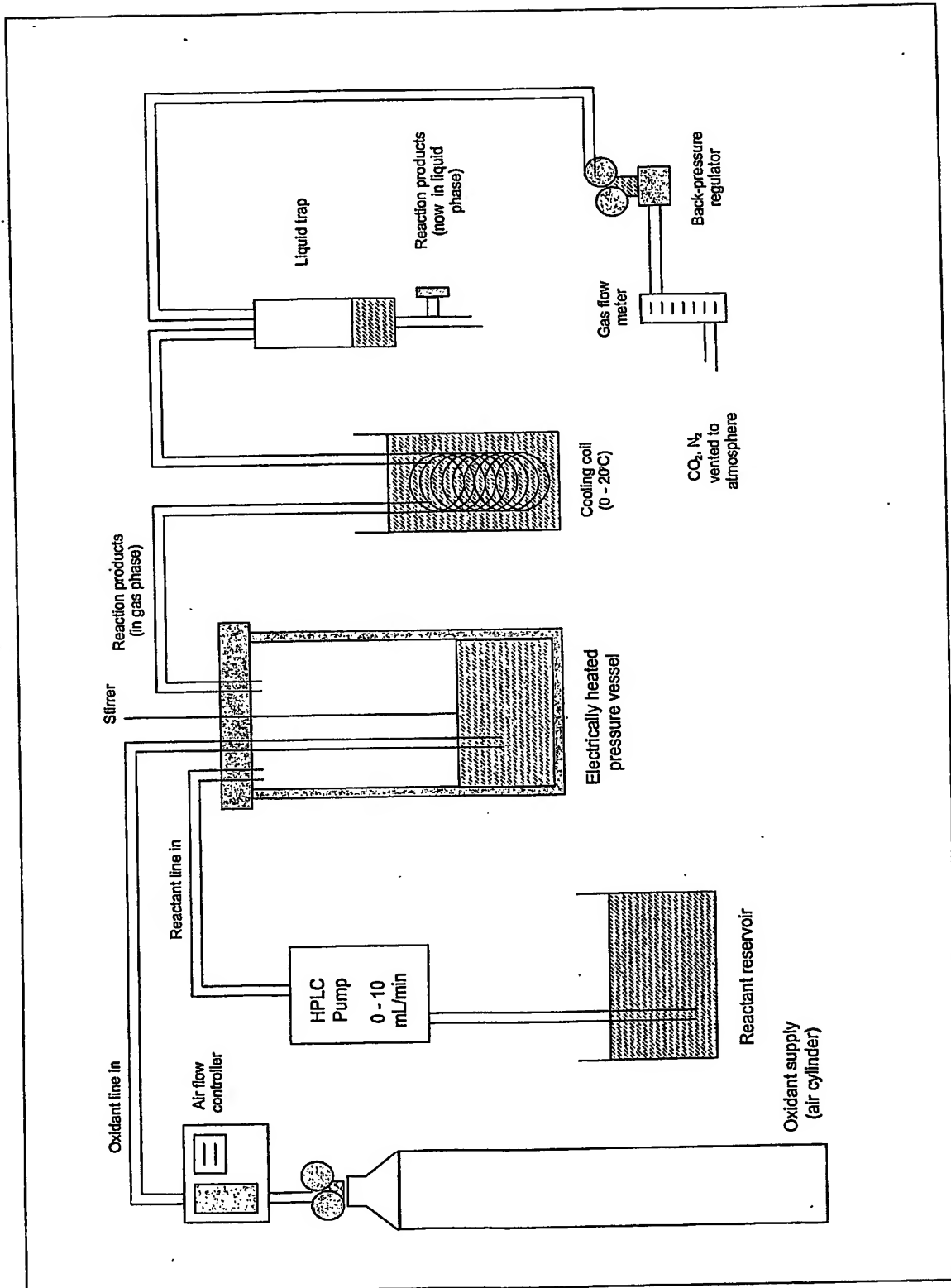


FIGURE 1

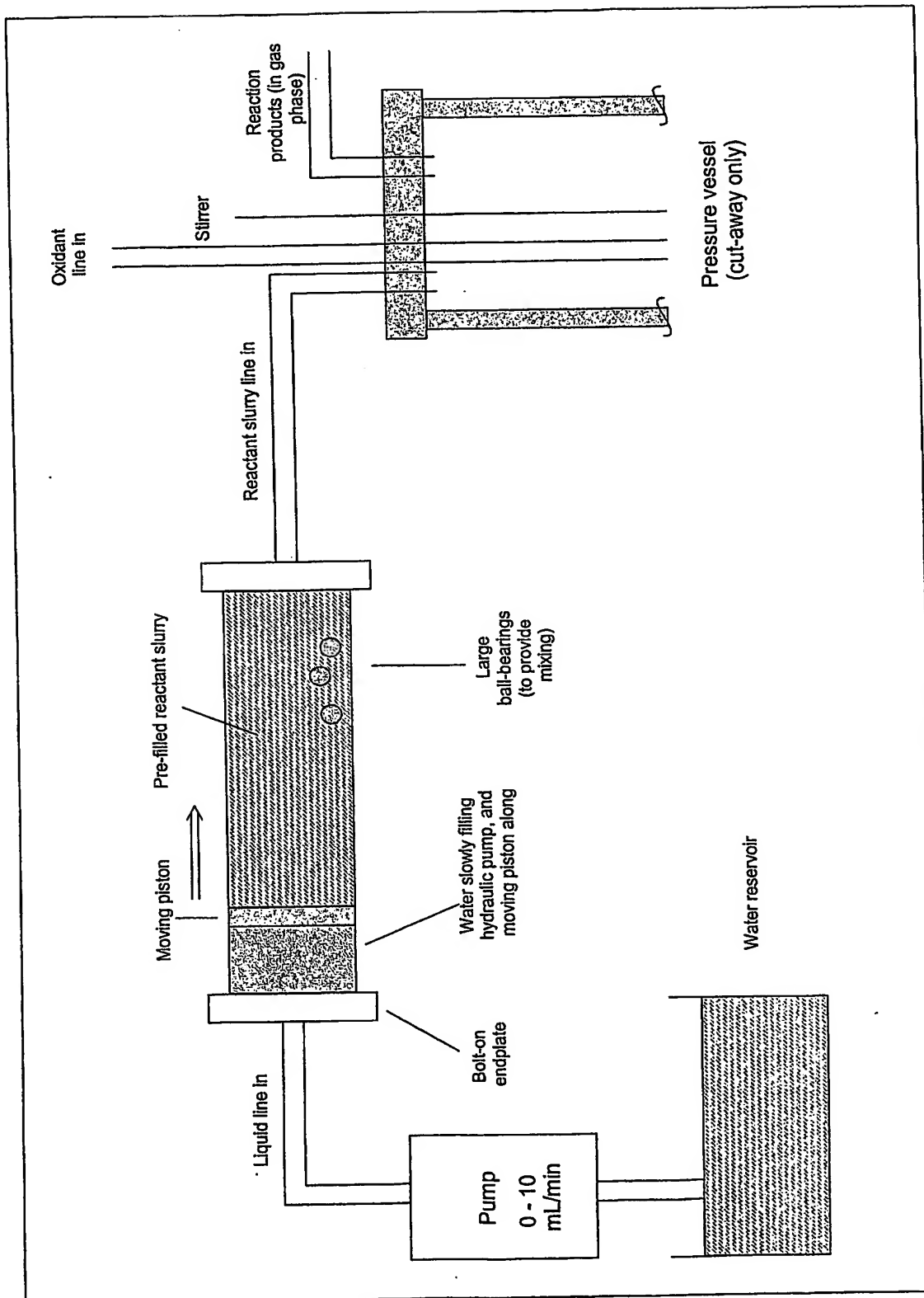


FIGURE 2

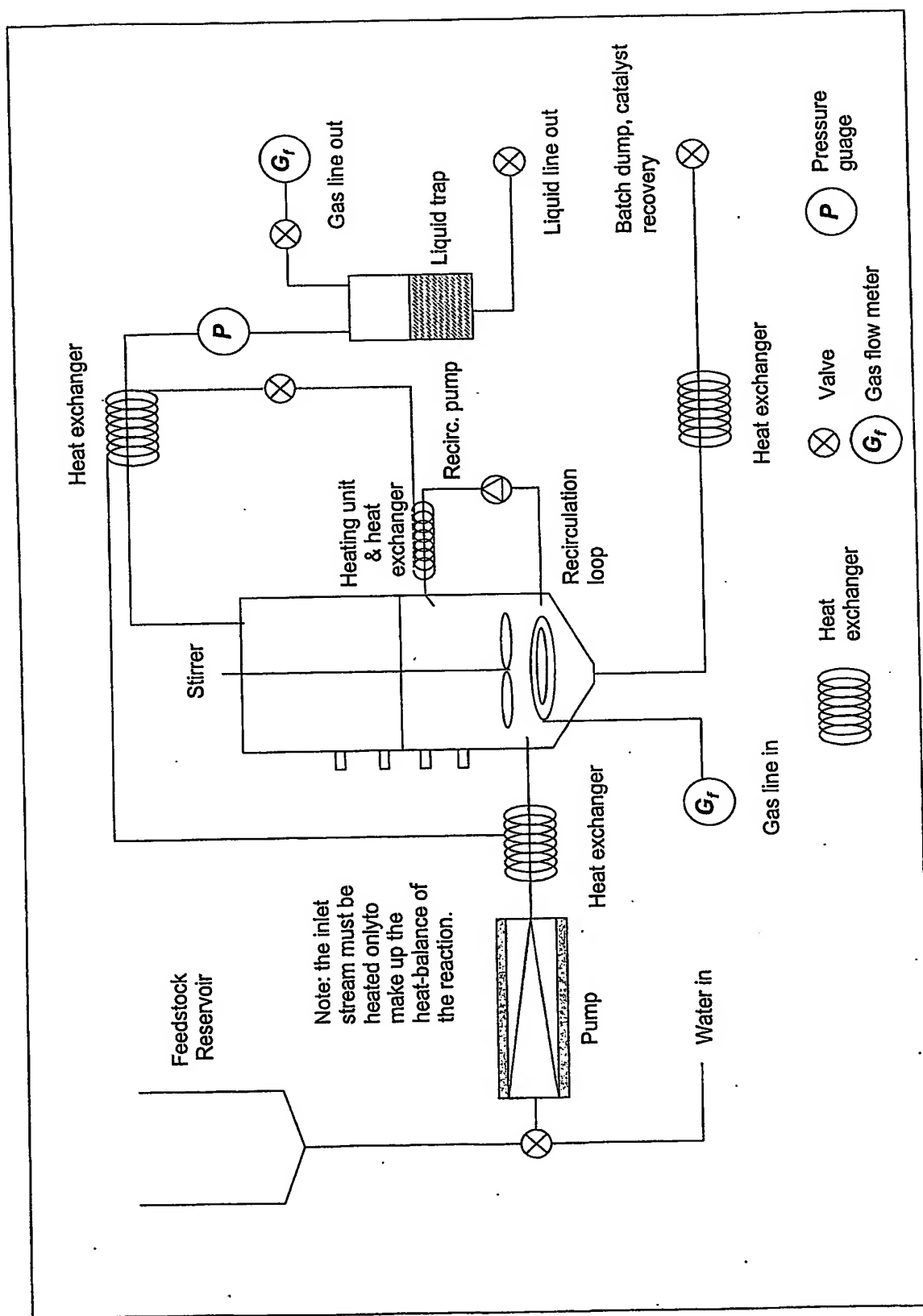


FIGURE 3

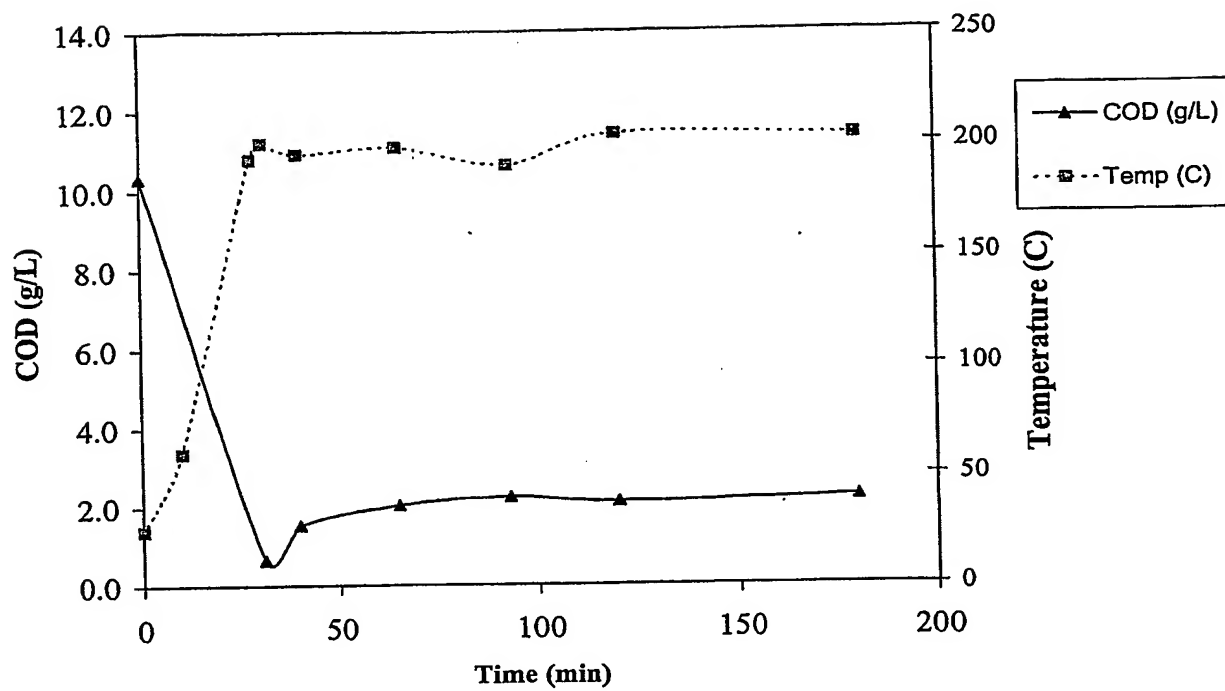


FIGURE 4

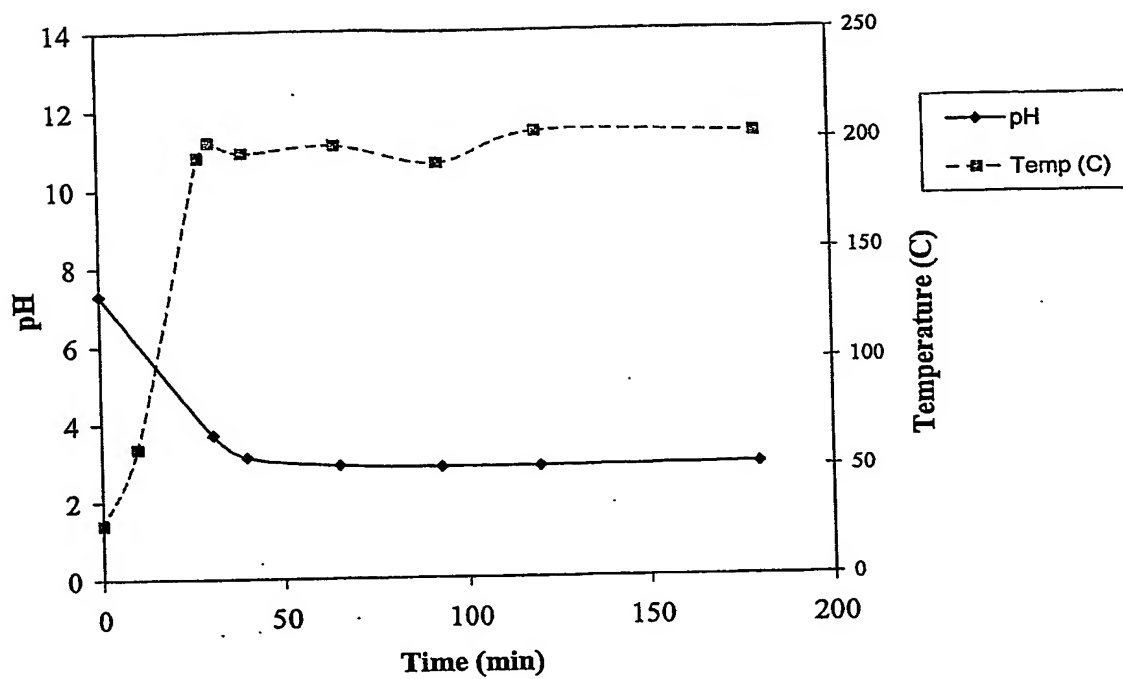


FIGURE 5

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